Journal of Ecology and Environmental Sciences
ISSN: 0976-9900 & E-ISSN: 0976-9919, Volume 6, Issue 1, 2015, pp.-137-142.
Available online at http://www.bioinfopublication.org/jouarchive.php?opt=&jouid=BPJ0000261

EVALUATION OF SPATIAL AND TEMPORAL VARIATIONS IN THE QUALITY OF WATER: A CASE STUDY OF SMALL STREAM IN POLAND

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Received: January 07, 2015; Revised: March 10, 2015; Accepted: March 12, 2015

Abstract- The aim of this study was to assess the physicochemical parameters of water of Rów Złotnicki, a small stream in Poland. The research was carried out throughout the year 2012. Samples were taken every month at 5 research stations situated at different points of the stream. Several parameters of water were measured *in situ* (pH, temperature, conductivity, dissolved oxygen). In addition, at each station, the volumetric flow rate was measured. Chemical analyses were made for nitrogen and phosphorus compounds using spectrophotometric methods. The results indicate variability in concentrations and loads of nutrients among the sites and dates of collecting the samples. The highest monthly phosphorus loads were observed in the second half of the year (in July and August). The approximate annual load equalled 15.5 kg. The highest concentrations out of the mineral form of nitrogen were reported for nitrates. The annual load of nitrate was over 996 kg. The highest monthly loads of total nitrogen were noted in the first half of year (from February to April). Nitrogen and phosphorus loads flowing into Strzeszyńskie Lake can deteriorate water quality and lead to its eutrophication.

Keywords- nitrogen and phosphorus, catchment area, Rów Złotnicki stream, water quality

Citation: Kaźmierska A. and Szeląg-Wasielewska E. (2015) Evaluation of Spatial and Temporal Variations in the Quality of Water: a Case Study of Small Stream in Poland. Journal of Ecology and Environmental Sciences, ISSN: 0976-9900 & E-ISSN: 0976-9919, Volume 6, Issue 1, pp.-137-142.

Introduction

A high rate of eutrophication and severity of trophic surface water, especially of lakes, have become a global issue [1,2]. Understanding the significance of the contribution of tributaries' nutrients in lakes may be the vital factor of successful water management [3]. The lake and its drainage basin constitute a basic, dynamic and functional system. Matter in the drainage basin is one of the forms of reservoir enrichment in terms of biogenic elements and compounds [4]. The intensity and quality of the matter flowing into a reservoir depend on several properties of the drainage basin. The most meaningful properties of the matter are permanent characteristics of the physical and geographical environment, such as the size and morphometry of the drainage basin, river network density, geological structure and soil conditions. Matter is also influenced by the use of land, which is a variable factor [5]. Nutrients can flow into surface waters from two types of sources: point and area sources. Area sources, including losses from the catchment area used for agriculture, are important for the nutrient balance [6,7].

In recent years, due to multidirectional human activities, the rate of the natural runoff of allochthonous matter from lands surrounding the lake has accelerated. Urbanization, industrialization, intensive agricultural production in the drainage basin, as well as a significant growth in tourism, all have an impact on phosphorus and nitrogen loads [8]. These loads can be excessive due to an increased amount of impervious surfaces, which increase surface runoff and reduce groundwater recharge. Rainwater sewage flowing into a reservoir causes disruption in the natural ecological balance of aquatic ecosystems [9-11]. The most common and most serious anthropogenic factor responsible for the disruption of functioning of aquatic ecosystems is eutrophication. Eutrophication might lead to enhanced primary production (increase in algae and cyanobacteria production), enhanced decay of the organic material and a shortage of oxygen [12].

The aim of this study was to determine the physicochemical parameters and describe seasonal changes in the quality of water of Rów Złotnicki stream, which flows into the Strzeszyńskie Lake. In addition, the impact of small streams on the quality of surface water was highlighted.

Study Site

Rów Złotnicki is a small watercourse (approx. 4 km long) which flows into the northern part of Strzeszyńskie Lake (Wielkopolska Region, Poland). This is the only tributary of the lake, which drains water off agricultural areas and collects rainwater from the nearby residential buildings. Its drainage basin amounts to 740.9 ha and comprises mainly built-up areas (approx. 20%), grassland (25.4%) and agricultural areas (34.9%). The main crops are rapeseed, winter rapeseed, corn, rye and triticale. In the upper part of the catchment dominate the built-up areas, in the middle the agriculture areas and in the lower part dominate the forest. The drainage basin of the stream is based in Poznań Commune (30%) and in the Suchy Las Commune (70%).

Strzeszyńskie Lake, which is of a post-glacial origin, is situated in the north-west part of the city of Poznań. Its area equals 34.9 ha, the maximum depth equals 17.8 m and the mean depth equals 8.2 m. Its shoreline is irregular at a length of 4.5 km [13]. Both the lake and the neighbouring areas are intensively used for recreational purposes [14]. The total 1115.8 ha of the drainage basin is extended to the north-east direction. The direct catchment of the lake is about 11 times larger than the lake's surface, and it is mainly covered by forests (45.7%), agricultural areas (27.9%) and meadows (10.8%).

Samples were taken at five research stations located in different points of Rów Złotnicki stream [Fig-1]: 1 - a station located in the point just ahead the rainwater reservoir (surface area of 1 ha) which collects water from Stary Las, 2 - a station situated behind the rainwater reservoir, after connecting tributaries from Stary Las, 3 - a station on a distributary of the stream from the rainwater reservoir located in Poznań, 4 - a station located in the short, periodically dry distributary of the stream, nearby Solei Hotel, 5 - a station located just before the stream flows into the lake, about 400 meters from a beach for tourists. The mean widths and depths measured at each of the stations were as follows: station 1 - 1.14 m, 0.16 m, station 2 - 1.43 m, 0.38 m, station 3 - 1.56 m, 0.23 m, station 4 - 0.2 m, 0.07 m, and station 5 - 0.67 m, 0.18 m, respectively.

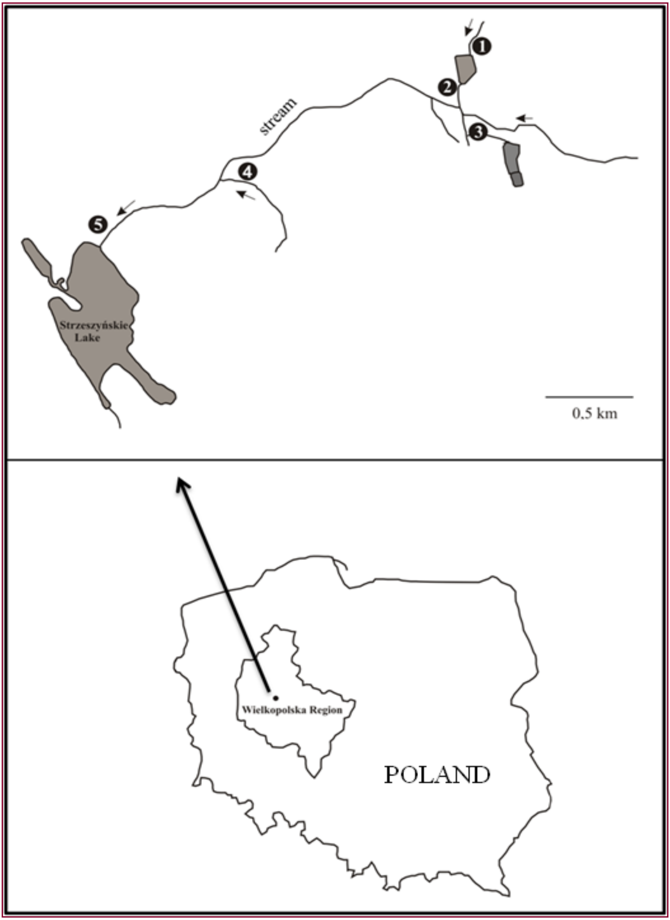

Fig. 1- The location of research stations nos. 1-5 at Rów Złotnicki stream

Methods

Analyses were carried out from January to December 2012. Once a month (27.01, 27.02, 27.03, 30.04, 21.05, 19.06, 23.07, 31.08, 27.09, 22.10, 20.11, 14.12), water samples were taken at five research stations. At each station, several parameters were measured *in situ*, such as: pH, water temperature, conductivity and dissolved oxygen levels. In addition, the volumetric flow rate was measured using an electromagnetic flow meter.

At each station, the samples used for the chemical analyses were collected and preserved with chloroform. The analyses, which included: phosphorus forms (total phosphorus - TP, total reactive phosphorus - TRP) and nitrogen forms (nitrates - NO_3, ammonium - NH_4, nitrites - NO_2), were conducted in accordance with the standard methods as described by Hermanowicz et al. [15] using a Cadas 200 UV-VIS (Dr Lange) spectrophotometer with a 5 cm or 1 cm glass cell against deionised water. Thus obtained nitrogen and phosphorus concentrations were compared to the Ordinance of the Minister of Environment [16] in order to determine the class of water quality [Table-1]. Statistical analyses were conducted using the STATISTICA 5.5 software. The Kruskal-Wallis H (KW-H) nonparametric tests were performed to compare obtained data.

Table 1- Limits of water quality indicators for surface water according to Ordinance of the Minister of Environment in Poland.

	limit of water quality indicator (adequate for the class)				
Indicator ($mg \cdot l^{-1}$)	I	II	III	IV	V
N-NH4	≤ 0.78	≤ 1.56	The limits are not established		
N-NO3	≤ 2.2	≤ 5			
Total nitrogen	≤ 5	≤ 10			
Total reactive phosporus	≤ 0.2	≤ 0.31			
Total phosphorus	≤ 0.2	≤ 0.4			

Results

The physical and chemical parameters of water samples collected at different sites and dates varied significantly. The pH of water was usually neutral or slightly alkaline [Table-2].

Table 2- The mean values, ranges and standard deviations (SD) of the selected characteristics of water at the stations of Rów Złotnicki stream throughout the year 2012.

	Station	pH	Temp. (ºC)	Conductivity ($\mu S \cdot cm$)	Oxygen ($mg \cdot L^{-1}$)
Ranges	1	7.2-8.4	0.7-18.9	96-1020	6.6-11.3
	2	6.9-8.1	0-23	275-790	5.7-14.6
	3	7.1-8.1	1.6-17	417-890	0.8-10.8
	4	7.8-8.4	0-19.4	550-730	6.5-9.3
	5	6.9-8.5	0-19.1	516-810	1.7-12.3
Mean±SD	1	7.8±0.3	12.2±6.5	667.6±265.5	8.3±1.6
	2	7.8±0.3	13.2±7.6	627.2±166	9.3±2.9
	3	7.7±0.3	11.8±6.5	677.5±144.4	4±3.5
	4	8.0±0.2	8.5±8.0	655±66.9	7.5±1.3
	5	7.9±0.4	10.7±7.4	675.8±92.2	8.1±2.7

The electrolytic conductivity of water was quite high, especially in the winter. The levels of dissolved oxygen were highest in the early spring and autumn, whereas in the summer these levels were very low, reaching only a few percent of saturation at the station no. 3. The flow rate fluctuated among the sites and seasons. The differences in the flow rate among the stations [Fig-2] were statistically significant (KW-H $_{(4;34)}$ = 10,4399; p< 0,05). The highest flow rate was noted during snowmelt and rain. It was impossible to measure the flow rate at the station no. 4 due to periods of stream drying. The flow rate at the station no. 3 was low throughout the year.

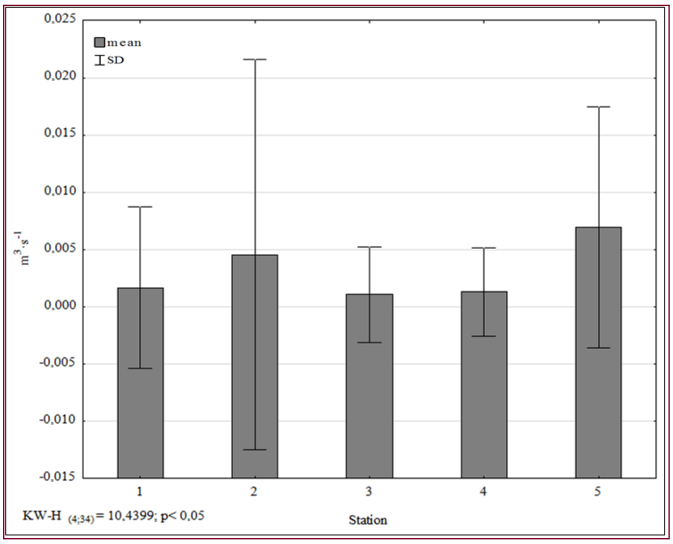

Fig. 2- Differences in the flow rate among the stations at Rów Złotnicki stream throughout the year 2012

Nitrate concentrations fluctuated from 0.04 mg·L^{-1} at the station no. 3 in July to 9.33 mg·L^{-1} at the station no. 4 in January. The highest nitrate concentrations were observed in the winter and autumn [Fig-3]. The lowest nitrate concentrations were observed at the stations no. 2 and 3, while at the station no. 4 the nitrate levels were always high. The differences in nitrate concentrations and loads between stations were statistically significant [Fig-4] and [Fig-5]. Despite the fact that the highest nitrate concentrations were observed at the station no. 4, nitrate loads were the highest at the station no. 5. The maximum daily nitrate load was noted in March (5.58 kg). Nitrite concentrations were low throughout the year and oscillated from 0.002 to 0.248 mg·L^{-1}. The highest nitrate concentrations were observed in March and April.

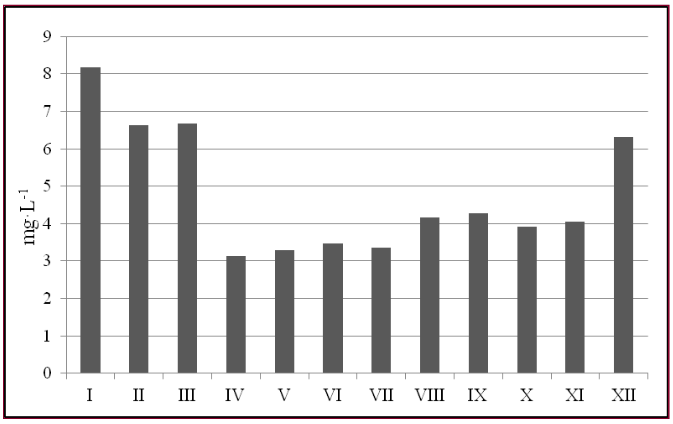

Fig. 3- Concentrations of NO$_3$ at the station no. 5 at Rów Złotnicki stream throughout the year 2012

The mean values of ammonium concentrations ranged from 0.368 mg·L^{-1} at the station no. 1 to 0.864 mg·L^{-1} at the station no. 2. The highest ammonium loads were noted at the stations no. 2 and 5 [Fig -6]. Organic nitrogen concentrations fluctuated from 0.2 mg·L^{-1} to 2.21 mg·L^{-1}. The highest levels were observed at the station no. 3 and the lowest ones at the stations no. 2 and 5. In March, July and September, the mean concentrations were higher than 1 mg·L^{-1} at all the stations. The highest organic nitrogen load (0.03 kg per day) was observed in September at the station no. 2.

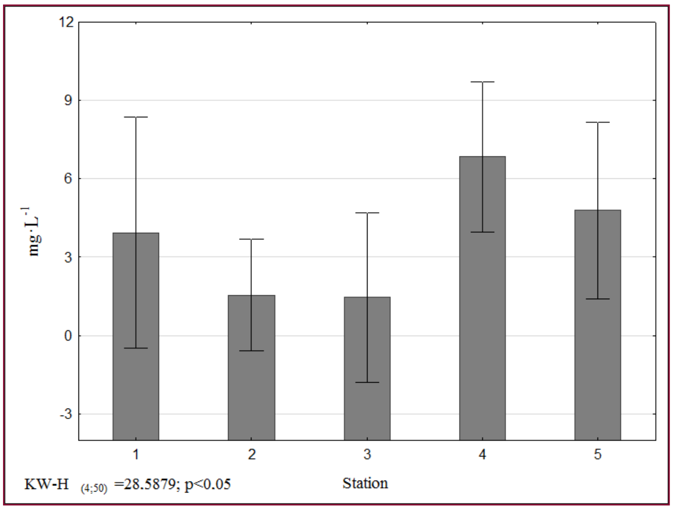

Fig. 4- Differences in NO$_3$ concentrations among the stations

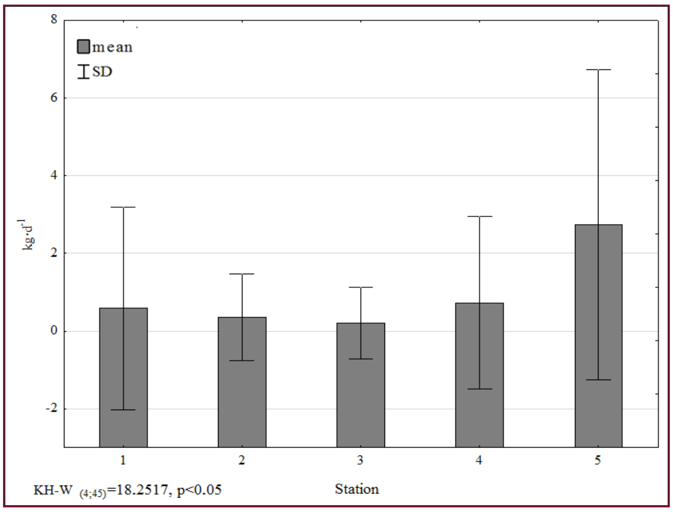

Fig. 5- Differences in NO$_3$ daily load among the stations at Rów Złotnicki stream throughout the year 2012

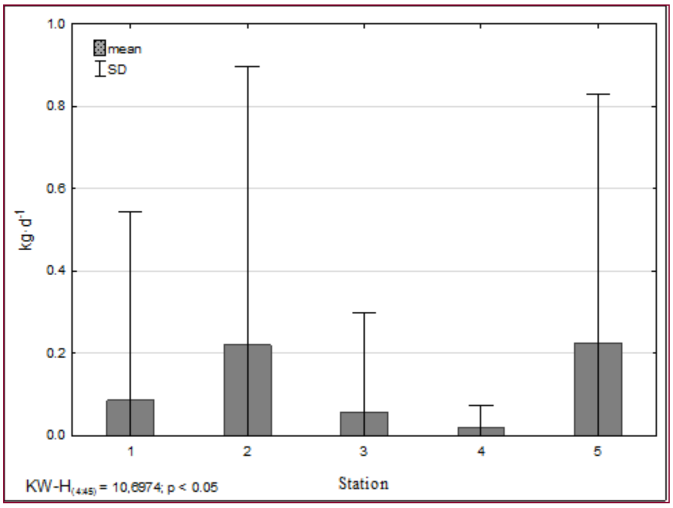

Fig. 6- Mean daily loads of NNH$_4^+$ at the stations

The highest total reactive phosphorus concentrations were noted at the station no. 3, especially in the autumn (from 0.21 to 0.31 mg·L^{-1}). At other stations, the mean concentrations were similar (ranging from 0.063 mg·L^{-1} at the station no. 5 to 0.068 mg·L^{-1} at the station no. 1). Nonetheless, the highest loads of the total reactive phosphorus were observed at the stations no. 2 and 5. The highest load was observed in August at the station no. 2 (0.16 kg per day). The total phosphorus concentrations were also high at the station no. 3, but the highest loads of the total reaction phosphorus were noted at the stations no. 2 and 5 (the mean values equalled to 0.047 and 0.046 kg per day, respectively). The highest level of the total phosphorus load was observed also in August at the station no. 2 (0.19 kg per day). The difference in the total phosphorus loads between stations was statistically significant [Fig-7].

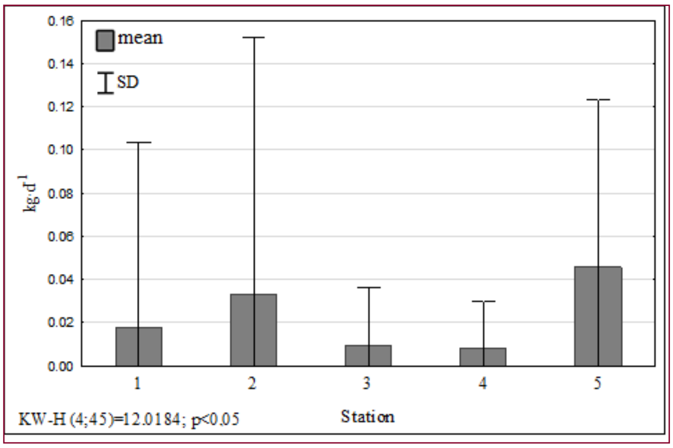

Fig. 7- The difference in total phosphorus daily loads among the stations

The concentrations and loads of analyzed chemical parameters varied depending on the point and date of samples collection. The highest loads of nitrogen and phosphorus compounds were observed at the station no. 5 due to the station's location just before the stream flows into the lake. The monthly loads of total phosphorus ranged from 0.2 to 3.19 kg [Fig-8]. The highest monthly phosphorus loads were noted in August and July and equalled 3.19 kg and 2.52 kg, respectively.

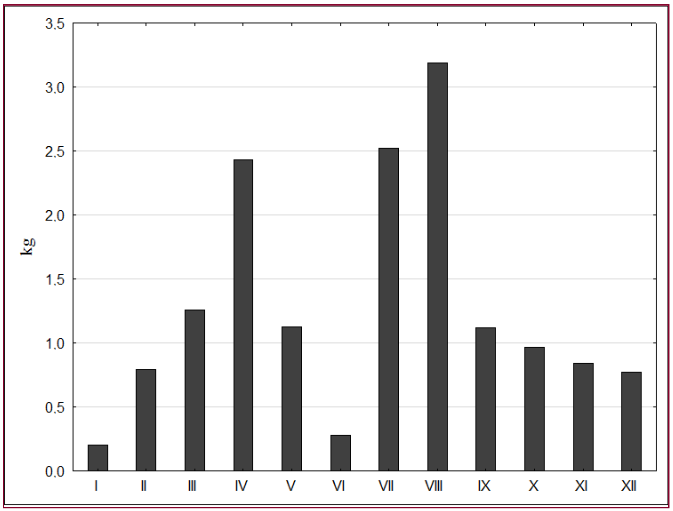

Fig. 8- The monthly loads of total phosphorus at the station no. 5

The approximate annual load equalled 15.5 kg. The monthly loads of nitrate were high throughout the year and equalled on average 83 kg. The annual load of nitrate was high, equalling over 996 kg. The monthly loads of nitrite were slightly lower and accounted for less than a kilogram, except for April and May. Furthermore, the monthly loads of ammonium varied significantly: from 0.83 kg in June to over 38 kg in December. The annual load of ammonium equalled 116 kg.

The monthly loads of total nitrogen at the station where the stream flows into the lake ranged from 7.56 kg in June to 248.76 kg in April [Fig-9]. The highest loads of nitrogen were noted in the winter. The annual load of nitrogen was high and amounted to 1,273.7 kg.

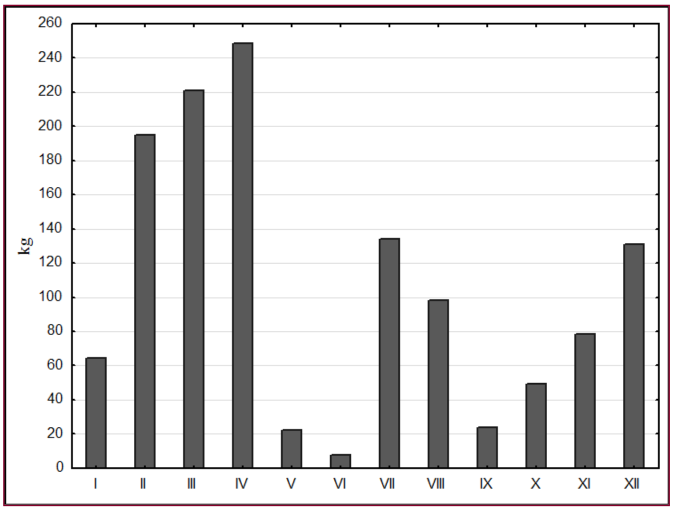

Fig. 9- The monthly loads of total nitrogen at the station no. 5

Discussion

The quality of surface water depends on the water quality of tributaries, including even the small ones, which are often left unrecognized. One of the main causes of degradation of aquatic ecosystems is an inadequate use of land, which affects both the physical and chemical characteristics of the surface water. Moreover, water quality is impacted by anthropogenic factors. Additionally, by removing the riparian vegetation, the natural protection against erosion is destroyed, which contributes to increasing the input of sediments, nutrients and other pollutants. [17]. Human activities, such as urban development, intensive agriculture, industry, and tourism, may cause an increase in phosphorus and nitrogen loads in watercourses, which in turn may have a serious impact on the water quality [18-20].

The drainage basin of Rów Złotnicki is mainly made of agriculture areas, which are its significant source of nutrients. There are a lot of factors affecting eluviations, such as configuration of terrain, soil permeability, methods of management, fertilization and water conditions [21]. In our study, nitrates levels, when compared to other nitrogen compounds, were the highest, which is the first symptom of pollution resulting from agricultural activities. In the summer, nitrates levels were lower, which could be ascribed to the growth of aquatic plants in the stream and its surroundings [22,23]. The highest nitrates levels were observed in the winter, which is a result of meltwater supply, characterized by increased contents of this form of nitrogen. This is also caused by the lack of vegetation and absence of fitosorption. Lower levels of nitrates in the agricultural catchment, which were observed during active plant growth, result from the depletion of readily available forms of nutrients in soil and water [24]. The influence of land use on the content of nutrients in the streams is scale-dependent and varies in time and space [3]. These compounds can reach the surface water in several ways, such as surface, subsurface and groundwater flows. For this reason, the time lag is also different: the shortest one is in the case of surface flow and the longest - in groundwater [25]. The relation between the land use and water quality has been already analysed in previous studies [26-29].

The level of ammonium nitrate did not show a seasonal pattern. The highest NH_4 levels were observed in the upper part of the stream at the stations no. 1 and 2, which could be connected with a larger share of a built area at this part of the catchment. The high amount of impervious surfaces leads to a decrease in infiltration and a higher volume of stormwater than from natural catchment of the equivalent area. Urban stormwater contains high concentrations of numerous pollutants, particularly bacterial contaminations [11,30]. Human and animal waste products constitute a major source of ammonium nitrate, which can flow into the stream as runoff from impervious surfaces [31]. This compound is an important member of the group of nitrogen - if its levels in surface water are too high, they can be toxic to some aquatic organisms. This can also affect other attributes of water, such as increasing biochemical oxygen demand and lowering dissolved oxygen levels. Dissolved oxygen levels can also be lowered when ammonium nitrogen is high due to an increased amount of nitrification [32]. In our study, the highest ammonium levels were noted at the station no, 3 - in the distributary of the rainwater reservoir, which was characterized by very low levels of dissolved oxygen.

The highest total phosphorus levels in water of Rów Złotnicki stream were observed in the second half of the year. Especially high levels of phosphorus were observed at the station no. 3 situated close to a sewage pumping station. The sources of phosphorus included agricultural fertilizers, urbanization, organic wastes in sewage, and manure [33-35]. An urban effect is most often seen in total phosphorus as a result of increased particle-associated phosphorus; nonetheless, dissolved phosphorus levels were also increased. The major factor contributing to flowing phosphorus into the stream from agricultural areas is soil erosion, as phosphorus is stored in soil as a product of fertilization. In addition, lawns and streets can be often an important source of phosphorus from urban area [30].

The results obtained for nitrite, nitrate and ammonium nitrite levels were significantly higher in comparison to other little watercourses in Poland, such as Brzezówka, Ratanica, or Trzemieśnianka (the catchment areas with significant share of agriculture, the size 420 ha, 160 ha and 2910 ha, respectively) [2]. In the Prądnik River (agriculture about 46% of the catchment area) [36], Dębnik and Wolnica (the size of catchment area 390 ha and 1550 ha, respectively) [2] only phosphorus concentrations were higher in comparison to the results obtained for Rów Złotnicki stream. The research conducted on thirteen streams in the United States [23] showed higher total phosphorus levels in urban streams than in the majority of forested streams. In all the above-mentioned studies, the total nitrogen and total phosphorus levels were lower in comparison to Rów Złotnicki stream. According to the Ordinance of the Minister of Environment (2011) regarding the classification of the quality of surface water [16], only phosphorus concentrations ranged mainly in first class of water quality. In respect to nitrate and ammonium levels, the quality of Rów Złotnicki's water can be categorized as a third class or lower. The results indicate that significant loads of nitrogen and phosphorus compounds flow from Rów Złotnicki to Strzeszyńskie Lake. This is a serious threat to the quality of the lake's water and can accelerate its eutrophication.

The water lakes are one of the most sensitive to human activities. This study looked at the impact of the quality of stream water on the quality of lake water. The study proves that even a small tributary can have a great impact on the lake that receives the tributary's water. In order to improve the quality of water and prevent degradation of the lake, an accurate diagnosis and decreasing the amount of pollution flowing into the lake are of key importance. Therefore, decidedly greater attention should be paid to monitoring and management of the lake.

The problem in catchment area of Rów Złotnicki stream is the lack of proper regulation of water and wastewater, especially rainwater runoff. Moreover, the buffer zones in the central part of catchment area should exist and the rational mineral and organic fertilisation (proper way, time and dose) should be respected.

Acknowledgements: The authors thank Mr Piotr Domek for technical assistance, Dr Tomasz Joniak for the help with conducting the chemical analyses and Dominik Kaźmierski for the help in the research of catchment area.

Conflicts of Interest: None declared.

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